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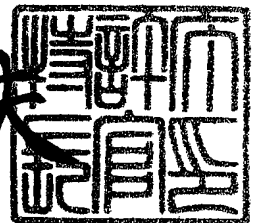
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[Title of the Invention] Positive electrode, non-aqueous electrolyte secondary battery, and method of manufacturing the same

5 [Scope of Claim for Patent]

[Claim 1] A method of manufacturing a positive electrode characterized by processing an electrode including elemental sulfur under reduced-pressure with the electrode immersed in a non-aqueous electrolyte, thereby impregnating
10 the electrode with the non-aqueous electrolyte.

[Claim 2] The method of manufacturing a positive electrode as recited in Claim 1, characterized in that a pressure during said reduced-pressure process is set to not higher than 28000 Pa.

15 [Claim 3] A positive electrode characterized by being manufactured by the method of manufacturing as recited in Claim 1 or 2.

[Claim 4] A method of manufacturing a non-aqueous electrolyte secondary battery characterized by preparing a
20 positive electrode by processing an electrode including elemental sulfur under reduced-pressure with the electrode immersed in a non-aqueous electrolyte.

[Claim 5] A non-aqueous electrolyte secondary battery characterized by comprising:

25 a positive electrode as recited in Claim 3;

a negative electrode; and

a non-aqueous electrolyte including a room temperature molten salt having a melting point of not higher than 60°C.

[Claim 6] The non-aqueous electrolyte secondary
5 battery as recited in Claim 5, characterized in that
said room temperature molten salt includes a quaternary ammonium salt.

[Claim 7] The non-aqueous electrolyte secondary
battery as recited in Claim 6, characterized in that
10 said quaternary ammonium salt includes at least one type
selected from the group consisting of
trimethylpropylammonium
bis(trifluoromethylsulfonyl)imide, trimethyloctylammonium
bis(trifluoromethylsulfonyl)imide, trimethylallylammonium
15 bis(trifluoromethylsulfonyl)imide, trimethylhexylammonium
bis(trifluoromethylsulfonyl)imide, trimethylethylammonium
2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide,
trimethylallylammonium
2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide,
20 trimethylpropylammonium
2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide,
tetraethylammonium
2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide, and
triethylmethylammonium
25 2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide.

[Claim 8] The non-aqueous electrolyte secondary battery as recited in any of Claims 5 to 7, characterized in that

said non-aqueous electrolyte includes at least one type
5 of solvent selected from the group consisting of cyclic ether, chain ether, and fluorinated carbonate.

[Claim 9] The non-aqueous electrolyte secondary battery as recited in Claim 8, characterized in that

said cyclic ether includes at least one type selected
10 from the group consisting of 1,3-dioxolane, 2-methyl-1,3-dioxolane, 4-methyl-1,3-dioxolane, tetrahydrofuran, 2-methyl tetrahydrofuran, propylene oxide, 1,2-butylene oxide, 1,4-dioxiane, 1,3,5-trioxane, furan, 2-methyl furan, 1,8-cineole, and crown ether; the chain ether
15 includes at least one type selected from the group consisting of 1,2-dimethoxyethane, diethyl ether, dipropyl ether, diisopropyl ether, dibutyl ether, dihexyl ether, ethyl vinyl ether, butyl vinyl ether, methyl phenyl ether, ethyl phenyl ether, butyl phenyl ether, pentyl phenyl ether,
20 methoxytoluene, benzyl ethyl ether, diphenyl ether, dibenzyl ether, o-dimethoxybenzene, 1,2-diethoxyethane, 1,2-dibutoxyethane, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, diethylene glycol dibutyl ether, 1,1-dimethoxymethane, 1,1-diethoxyethane,
25 triethylene glycol dimethyl ether, and tetraethylene glycol

dimethyl ether; and the fluorinated carbonate includes at least one type selected from the group consisting of trifluoropropylene carbonate and fluoroethyl carbonate.

[Claim 10] The non-aqueous electrolyte secondary
5 battery as recited in any of Claims 5 to 9, characterized in that

a conductive agent is added to said positive electrode.

[Claim 11] The non-aqueous electrolyte secondary
battery as recited in any of Claims 5 to 10, characterized
10 in that

said negative electrode includes a carbon material or a silicon material.

[Detailed Description of the Invention]

[0001]

15 [Technical Field to which the Invention Belongs]

The present invention relates to a positive electrode, non-aqueous electrolyte secondary battery comprising the positive electrode, and method of manufacturing the same.

[0002]

20 [Conventional Art]

Non-aqueous electrolyte secondary batteries have been used as secondary batteries having high energy densities. A non-aqueous electrolyte secondary battery employing a non-aqueous electrolyte is charged and discharged by the

transport of lithium ions between positive and negative electrodes.

[0003]

Conventionally, such a non-aqueous electrolyte
5 secondary battery typically employs, as a positive electrode,
a lithium transition metal mixed oxide such as LiCoO_2 ; as a
negative electrode, lithium metal, a lithium alloy, or a
carbon material that can store lithium and release it. The
battery has a non-aqueous electrolyte including an
10 electrolyte salt of a lithium salt, such as LiBF_4 and LiPF_6 ,
dissolved in an organic solvent of ethylene carbonate,
diethyl carbonate, or the like.

[0004]

Such a non-aqueous electrolyte secondary battery has
15 recently been used as a power source for a variety of mobile
equipment, and therefore, a need exists for a non-aqueous
electrolyte secondary battery with higher energy density.

[0005]

However, a lithium transition metal mixed oxide such as
20 LiCoO_2 , employed for the positive electrode in a conventional
non-aqueous electrolyte secondary battery, is large in weight
with the small number of reaction electrons. This makes it
difficult to sufficiently increase capacity per unit weight.

[0006]

Conventionally, sulfur has been known as a positive electrode material having a large theoretical capacity. However, elemental sulfur used in the positive electrode requires high temperature to be reversibly reacted with
5 lithium, making it impossible to make the non-aqueous electrolyte secondary battery available for general use.
[0007]

In recent years, the use of an organic disulfide compound, such as DMcT (2,5-dimercapto-1,3,4-thiadiazole),
10 as a positive electrode material for achieving high capacity and high energy density has been proposed. However, the organic disulfide compound used as a positive electrode material react reversibly with lithium only at elevated temperatures of 60°C or higher. Therefore, the use of organic
15 disulfide compound in general non-aqueous electrolyte secondary batteries has been difficult.
[0008]

Moreover, in recent years, a secondary battery has been proposed capable of the charge-discharge reaction at room
20 temperature using a positive electrode material obtained from the above-mentioned organic disulfide compound, such as DMcT, mixed with a conductive polymer, such as polyaniline (refer to Patent Document 1 or 2.)

[0009]

25 [Patent Document 1]

JP-4-267073-A

[Patent Document 2]

JP-8-115724-A

[0010]

5 [Problems to be Solved by the Invention]

In the case of the above-mentioned positive electrode active material using the organic disulfide compound, however, the disulfide bonds are involved with the charge-discharge reaction, and other parts including carbon
10 atoms and hydrogen atoms do not contribute to the reaction. Therefore, it has been difficult to further increase a capacity per weight.

[0011]

Accordingly, it is desired that high energy density is
15 obtained by the use of elemental sulfur having a high theoretical capacitance as a positive electrode material.

[0012]

An object of the present invention is to provide a method of manufacturing a positive electrode having increased energy
20 density by the use of elemental sulfur and a non-aqueous electrolyte secondary battery comprising the same.

[0013]

Another object of the present invention is to provide a positive electrode and a non-aqueous electrolyte secondary

battery having increased energy densities by the use of elemental sulfur.

[0014]

[Means for Solving the Problems and Effects of the Invention]

5 A method of manufacturing a positive electrode according to a first invention is processing an electrode including elemental sulfur under reduced-pressure with the electrode immersed in a non-aqueous electrolyte, thereby impregnating the electrode with the non-aqueous electrolyte.

10 [0015]

 In the method of manufacturing the positive electrode according to the present invention, the electrode including elemental sulfur can be sufficiently impregnated with the non-aqueous electrolyte. Accordingly, also in a non-aqueous
15 electrolyte secondary battery using a positive electrode including elemental sulfur, the charging/discharging reaction can be carried out at room temperature, and much increased energy density can be achieved.

[0016]

20 A pressure during the reduced-pressure process may be set to not higher than 28000 Pa (- 55 cmHg with respect to atmospheric pressure). This allows the electrode including elemental sulfur to be more sufficiently impregnated with the non-aqueous electrolyte.

25 [0017]

A positive electrode according to a second invention is manufactured by the method of manufacturing according to the first invention.

[0018]

5 In the positive electrode according to the present invention, because the electrode including elemental sulfur is sufficiently impregnated with the electrolyte, the charging/discharging reaction can be carried out at room temperature, and much increased energy can be achieved, when
10 used in a non-aqueous electrolyte secondary battery.

[0019]

A method of manufacturing a non-aqueous electrolyte secondary battery according to a third invention is preparing a positive electrode by processing an electrode including
15 elemental sulfur under reduced-pressure with the electrode immersed in a non-aqueous electrolyte.

[0020]

In the method of manufacturing the non-aqueous electrolyte secondary battery according to the present
20 invention, a non-aqueous electrolyte secondary battery comprising a positive electrode including elemental sulfur sufficiently impregnated with a non-aqueous electrolyte can be manufactured. This enables the charging/discharging reaction to be carried out at room temperature, and much
25 increased energy density can be achieved.

[0021]

A non-aqueous electrolyte secondary battery according to a fourth invention comprises a positive electrode according to the second invention; a negative electrode; and
5 a non-aqueous electrolyte including a room temperature molten salt having a melting point of not higher than 60°C.

[0022]

In the non-aqueous electrolyte secondary battery according to the present invention, because the electrode
10 including elemental sulfur constituting the positive electrode is sufficiently impregnated with the non-aqueous electrolyte, and the non-aqueous electrolyte includes the room temperature molten salt having a melting point of not higher than 60°C, the charging/discharging reaction can be
15 carried out at room temperature, and much increased energy density can be achieved.

[0023]

The room temperature molten salt may include a quaternary ammonium salt.

20 The quaternary ammonium salt may include at least one type selected from the group consisting of trimethylpropylammonium bis(trifluoromethylsulfonyl)imide ($(\text{CH}_3)_3\text{N}^+(\text{C}_3\text{H}_7)\text{N}^-(\text{SO}_2\text{CF}_3)_2$), trimethyloctylammonium bis(trifluoromethylsulfonyl)imide
25 ($(\text{CH}_3)_3\text{N}^+(\text{C}_8\text{H}_{17})\text{N}^-(\text{SO}_2\text{CF}_3)_2$), trimethylallylammonium

bis(trifluoromethylsulfonyl)imide

$((\text{CH}_3)_3\text{N}^+(\text{Allyl})\text{N}^-(\text{SO}_2\text{CF}_3)_2)$, trimethylhexylammonium

bis(trifluoromethylsulfonyl)imide

$((\text{CH}_3)_3\text{N}^+(\text{C}_6\text{H}_{13})\text{N}^-(\text{SO}_2\text{CF}_3)_2)$, trimethylethylammonium

5 2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide

$((\text{CH}_3)_3\text{N}^+(\text{C}_2\text{H}_5)(\text{CF}_3\text{CO})\text{N}^-(\text{SO}_2\text{CF}_3))$, trimethylallylammonium

2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide

$((\text{CH}_3)_3\text{N}^+(\text{Allyl})(\text{CF}_3\text{CO})\text{N}^-(\text{SO}_2\text{CF}_3))$, trimethylpropylammonium

2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide

10 $((\text{CH}_3)_3\text{N}^+(\text{C}_3\text{H}_7)(\text{CF}_3\text{CO})\text{N}^-(\text{SO}_2\text{CF}_3))$, tetraethylammonium

2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide

$((\text{C}_2\text{H}_5)_4\text{N}^+(\text{CF}_3\text{CO})\text{N}^-(\text{SO}_2\text{CF}_3))$, and triethylmethylammonium

2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide

$((\text{C}_2\text{H}_5)_3\text{N}^+(\text{CH}_3)(\text{CF}_3\text{CO})\text{N}^-(\text{SO}_2\text{CF}_3))$.

15 [0024]

The non-aqueous electrolyte may include at least one type of solvent selected from the group consisting of cyclic ethers, chain ethers, and fluorinated carbonates.

[0025]

20 The cyclic ether may include at least one type selected

from the group consisting of 1,3-dioxolane,

2-methyl-1,3-dioxolane, 4-methyl-1,3-dioxolane,

tetrahydrofuran, 2-methyl tetrahydrofuran, propylene oxide,

1,2-butylene oxide, 1,4-dioxane, 1,3,5-trioxane, furan,

25 2-methy furan, 1,8-cineole, and crown ether.

[0026]

The chain ether may include at lest one type selected from the group consisting of 1,2-dimethoxyethane, diethyl ether, dipropyl ether, diisopropyl ether, dibutyl ether, dihexyl ether, ethyl vinyl ether, butyl vinyl ether, methyl phenyl ether, ethyl phenyl ether, butyl phenyl ether, pentyl phenyl ether, methoxytoluene, benzyl ethyl ether, diphenyl ether, dibenzyl ether, o-dimethoxybenzene, 1,2-diethoxyethane, 1,2-dibutoxyethane, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, diethylene glycol dibutyl ether, 1,1-dimethoxymethane, 1,1-diethoxyethane, triethylene glycol dimethyl ether, and tetraethylene glycol dimethyl ether.

[0027]

The fluorinated carbonate may include at least one type selected from the group consisting of trifluoropropylene carbonate and fluoroethyl carbonate.

[0028]

A conductive agent may be added to the positive electrode. This enhances the conductivity of the positive electrode. As a result, the charging-discharging characteristics can be enhanced.

[0029]

The negative electrode may include a carbon material or a silicon material. In particular, in the case of the negative

electrode including a silicon material, further increased energy density can be achieved.

[0030]

[Embodiments of the Invention]

5 Description will then be made of a non-aqueous electrolyte secondary battery according to an embodiment of the present invention and method of manufacturing the same.

[0031]

10 The non-aqueous electrolyte secondary battery according to the present embodiment comprises a negative electrode, a positive electrode, and a non-aqueous electrolyte.

[0032]

15 The positive electrode has a positive electrode active material made of a mixture of elemental sulfur, a conductive agent, and a binder. The electrode having the positive electrode active material is subjected to reduced-pressure process while immersed in the non-aqueous electrolyte. A pressure during the reduced-pressure process is preferably
20 not higher than 28000 Pa (-55 cmHg with respect to atmospheric pressure.) This allows the electrode including elemental sulfur to be sufficiently impregnated with the non-aqueous electrolyte.

[0033]

As the conductive agent, a conductive carbon material, for example, may be used. It is noted that addition of too small an amount of conductive carbon material cannot sufficiently enhance the conductivity in the positive
5 electrode, whereas addition of an excessive amount of the material decreases the ratio of elemental sulfur in the positive electrode, and fails to achieve high capacity. Accordingly, the amount of carbon material may be set in the range of 5 to 84% by weight of the whole positive electrode
10 active material, preferably, in the range of 5 to 54% by weight, more preferably, in the range of 5 to 20% by weight.
[0034]

As the negative electrode, a carbon material, such as graphite, capable of storage and release of Li (lithium), Li
15 metal, Li alloy, or the like is used.
[0035]

Silicon that stores lithium may also be used as the negative electrode. For example, an amorphous silicon thin film or a microcrystalline silicon film may be formed on a
20 current collector made of a copper foil or the like having an electrolytically treated surface. A thin film made of a mixture of amorphous silicon and microcrystalline silicon may also be used. As a film formation method, sputtering, plasma CVD (chemical vapor deposition), or the like may be used. In
25 particular, it is preferable to use silicon with large

capacity, as proposed in JP-2001-266851-A and JP-2002-83594-A (or WO01/029912.) This enables a non-aqueous electrolyte secondary battery having increased energy density.

5 [0036]

In the non-aqueous electrolyte secondary battery according to the present embodiment, lithium involving the charge-discharge reaction is held either in the above-mentioned positive electrode or negative electrode.

10 [0037]

As the non-aqueous electrolyte, a non-aqueous electrolyte including a room temperature molten salt having a melting point of not higher than 60°C and a lithium salt may be used, as in the first embodiment. The room temperature molten salt is a liquid containing only ions, having fire-resistance and no vapor pressure, and therefore, they are not decomposed or burned even at the time of abnormal operations, such as overcharging, and can be safely used without the provision of a protection circuit or the like.

20 [0038]

It is necessary for the room temperature molten salt to remain liquid in a broad room temperature range, in general, in the range of -20°C to 60°C. It is desired that the room temperature molten salt have a conductivity of not less than 10^{-4} S/cm.

[0039]

By the addition of a lithium salt, a room temperature molten salt will probably have a lower melting point than the melting point of each of the two types of salts alone, and
5 these are maintained in a liquid state.

[0040]

As the non-aqueous electrolyte salt, a non-aqueous electrolyte salt including a quaternary ammonium salt and a lithium salt may also be used.

10 [0041]

The non-aqueous electrolyte may further include an organic solvent in addition to the room temperature molten salt having a melting point of not higher than 60°C and the lithium salt.

15 [0042]

As the room temperature molten salt, a quaternary ammonium salt or an imidazolium salt may be used, for example. Specifically, as the room temperature molten salt, at least one type selected from trimethylpropylammonium

20 bis(trifluoromethylsulfonyl)imide

$((\text{CH}_3)_3\text{N}^+(\text{C}_3\text{H}_7)\text{N}^-(\text{SO}_2\text{CF}_3)_2)$, trimethyloctylammonium

bis(trifluoromethylsulfonyl)imide

$((\text{CH}_3)_3\text{N}^+(\text{C}_8\text{H}_{17})\text{N}^-(\text{SO}_2\text{CF}_3)_2)$, trimethylallylammonium

bis(trifluoromethylsulfonyl)imide

25 $((\text{CH}_3)_3\text{N}^+(\text{Allyl})\text{N}^-(\text{SO}_2\text{CF}_3)_2)$, trimethylhexylammonium

bis(trifluoromethylsulfonyl)imide
 $((\text{CH}_3)_3\text{N}^+(\text{C}_6\text{H}_{13})\text{N}^-(\text{SO}_2\text{CF}_3)_2)$, trimethylethylammonium
 2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide
 $((\text{CH}_3)_3\text{N}^+(\text{C}_2\text{H}_5)(\text{CF}_3\text{CO})\text{N}^-(\text{SO}_2\text{CF}_3))$, trimethylallylammonium
 5 2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide
 $((\text{CH}_3)_3\text{N}^+(\text{Allyl})(\text{CF}_3\text{CO})\text{N}^-(\text{SO}_2\text{CF}_3))$, trimethylpropylammonium
 2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide
 $((\text{CH}_3)_3\text{N}^+(\text{C}_3\text{H}_7)(\text{CF}_3\text{CO})\text{N}^-(\text{SO}_2\text{CF}_3))$, tetraethylammonium
 2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide
 10 $((\text{C}_2\text{H}_5)_4\text{N}^+(\text{CF}_3\text{CO})\text{N}^-(\text{SO}_2\text{CF}_3))$, triethylmethylanmonium
 2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide
 $((\text{C}_2\text{H}_5)_3\text{N}^+(\text{CH}_3)(\text{CF}_3\text{CO})\text{N}^-(\text{SO}_2\text{CF}_3))$,
 1-ethyl-3-methylimidazolium
 bis(pentafluoroethylsulfonyl)imide
 15 $((\text{C}_2\text{H}_5)(\text{C}_3\text{H}_3\text{N}_2)^+(\text{CH}_3)\text{N}^-(\text{SO}_2\text{C}_2\text{F}_5)_2)$,
 1-ethyl-3-methylimidazolium
 bis(trifluoromethylsulfonyl)imide
 $((\text{C}_2\text{H}_5)(\text{C}_3\text{H}_3\text{N}_2)^+(\text{CH}_3)\text{N}^-(\text{SO}_2\text{CF}_3)_2)$,
 1-ethyl-3-methylimidazolium tetrafluoroborate
 20 $((\text{C}_2\text{H}_5)(\text{C}_3\text{H}_3\text{N}_2)^+(\text{CH}_3)\text{BF}_4^-)$, 1-ethyl-3-methylimidazolium
 pentafluoroborate $((\text{C}_2\text{H}_5)(\text{C}_3\text{H}_3\text{N}_2)^+(\text{CH}_3)\text{PF}_6^-)$, and the like.
 [0043]

It is presumed that the same effects are obtained when
 a non-aqueous electrolyte including at least one type
 25 selected from tetramethylammonium tetrafluoroborate

$((\text{CH}_3)_4\text{N}^+\text{BF}_4^-)$, tetramethylammonium hexafluorophosphate
 $((\text{CH}_3)_4\text{N}^+\text{PF}_6^-)$, tetraethylammonium tetrafluoroborate
 $((\text{C}_2\text{H}_5)_4\text{N}^+\text{BF}_4^-)$, tetraethylammonium hexafluorophosphate
 $((\text{C}_2\text{H}_5)_4\text{N}^+\text{PF}_6^-)$, and the like as the quaternary ammonium salt,
5 instead of the above-mentioned quaternary ammonium salt for
use as a room temperature molten salt is used.

[0044]

It is noted that the above-mentioned non-aqueous
electrolyte may include an organic solvent, such as ethylene
10 carbonate, diethyl carbonate, dimethyl carbonate, propylene
carbonate, cyclic ether, chain ether, fluorinated carbonate,
in addition to the room temperature molten salt.

[0045]

As the cyclic ether, at least one type selected from
15 1,3-dioxolane, 2-methyl-1,3-dioxolane,
4-methyl-1,3-dioxolane, tetrahydrofuran, 2-methyl
tetrahydrofuran, propylene oxide, 1,2-butylene oxide,
1,4-dioxane, 1,3,5-trioxane, furan, 2-methyl furan,
1,8-cineole, crown ether, and the like may be used.

20 [0046]

As the chain ether, at least one type selected from
1,2-dimethoxyethane, diethyl ether, dipropyl ether,
diisopropyl ether, dibutyl ether, dihexyl ether, ethyl vinyl
ether, butyl vinyl ether, methyl phenyl ether, ethyl phenyl
25 ether, butyl phenyl ether, pentyl phenyl ether,

methoxytoluene, benzyl ethyl ether, diphenyl ether, dibenzyl ether, o-dimethoxybenzene, 1,2-diethoxyethane, 1,2-dibutoxyethane, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, diethylene glycol dibutyl ether, 1,1-dimethoxymethane, 1,1-diethoxyethane, triethylene glycol dimethyl ether, tetraethylene glycol dimethyl ether, and the like may be used. As the fluorinated carbonate, at least one type selected from trifluoropropylene carbonate, fluoroethyl carbonate, and the like may be used.

10 [0047]

As the lithium salt to be added to the non-aqueous electrolyte, a lithium salt used as an electrolyte in general non-aqueous electrolyte secondary battery may be used. For example, at least one type selected from LiBF_4 , LiPF_6 , LiCF_3SO_3 , $\text{LiC}_4\text{F}_9\text{SO}_3$, $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$, $\text{LiN}(\text{CF}_3\text{SO}_2)(\text{COCF}_3)$, and LiAsF_6 may be used.

[0048]

In the non-aqueous electrolyte secondary battery according to the present embodiment, the above-mentioned use of intact elemental sulfur in the positive electrode allows further increased capacity per unit weight than that obtained using an organic disulfide compound. Moreover, the electrode having elemental sulfur can be sufficiently impregnated with the non-aqueous electrolyte because the electrode having the positive electrode active material is subjected to the

reduced-pressure process while immersed in the non-aqueous electrolyte. Consequently, also in a non-aqueous electrolyte secondary battery using a positive electrode including elemental sulfur, the charge-discharge reaction can be
5 carried out at room temperature, and the energy density can be much increased.

[0049]

(Example)

It will now be apparent from the citation of Examples
10 that the non-aqueous electrolyte secondary battery according to the present invention having a positive electrode using elemental sulfur can be appropriately charged/discharged at room temperature, and has much increased energy density. It will be recognized that the following examples merely
15 illustrate the practice of the non-aqueous electrolyte secondary battery in the present invention but are not intended to be limiting thereof. Suitable changes and modifications can be effected without departing the scope of the present invention.

20 [0050]

In each of the following Inventive Example and Comparative Example, the test cell shown in Fig. 1 was prepared to evaluate the positive electrode including sulfur material.

25 [0051]

As shown in Fig. 1, the non-aqueous electrolyte 14 was poured into the test cell vessel 10, and the working electrode 11, counter electrode 12, and reference electrode 13 were immersed in the non-aqueous electrolyte 14.

5 [0052]

(Comparative Example)

For a positive electrode, 75% by weight of sulfur powder with a purity of 99%, 20% by weight of kitchen black as a conductive agent, 4% by weight of styrene-butadiene rubber
10 as a binder, and 1% by weight of carboxymethylcellulose as a thickener were mixed with the addition of water, and further mixed in a mortar to prepare slurry. The slurry was applied on an electrolytic aluminum foil by doctor blade technique, and cut into a 2 cm x 2 cm size to make an electrode. The
15 electrode was dried under vacuum at 50°C to prepare the positive electrode.

[0053]

A non-aqueous electrolyte including a lithium salt, $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ dissolved at a concentration of 0.5 mol/l in a
20 mixture of 1,3-dioxolane and trimethylpropylammonium bis(trifluoromethylsulfonyl)imide $((\text{CH}_3)_3\text{N}^+(\text{C}_3\text{H}_7)\text{N}^-(\text{SO}_2\text{CF}_3)_2)$ with a volume ratio of 10:90 was used.

[0054]

Then, as shown in Fig. 1, the above-mentioned
25 non-aqueous electrolyte 14 was poured into the test cell

vessel 10, while the positive electrode was used as the working electrode 11, and lithium metal was used for each of the negative electrode as the counter electrode 12 and the reference electrode 13, to prepare a test cell of Comparative Example.

[0055]

The test cell of Comparative Example was discharged to a discharge cutoff potential of 1.5 V (vs. Li/Li⁺) at a discharge current of 0.05 mA/cm², and then charged to a charge cutoff potential of 2.8 V (vs. Li/Li⁺) at a charge current of 0.05 mA/cm², to examine the initial charge-discharge characteristics. The results are given in Fig. 2.

[0056]

Note that the solid line represents a discharge curve showing the relationship between the potential and the specific capacity per 1 g of elemental sulfur during discharging, and the broken line represents a charge curve showing the relationship between the potential and the specific capacity per 1 g of elemental sulfur during charging.

[0057]

The initial discharge and charge specific capacities were 144 mAh/g, and 130 mAh/g, respectively. This suggests that the elemental sulfur was charged/discharged reversibly.

[0058]

(Inventive Example)

The test cell of Inventive Example was prepared in a similar way as the test cell of Comparative Example. Further, in order to facilitate the impregnation of the positive electrode with the electrolyte, the test cell vessel 10 was held under a pressure of 28000 Pa (- 55 cmHg with respect to atmospheric pressure) for 30 minutes.

[0059]

The test cell of Inventive Example was discharged to a discharge cutoff potential of 1.5 V (vs. Li/Li⁺) at a discharge current of 0.05 mA/cm², and then charged to a charge cutoff potential of 2.8 V (vs. Li/Li⁺) at a charge current of 0.05 mA/cm², to examine the initial charge-discharge characteristics. The results are given in Fig. 3.

[0060]

Note that the solid line represents a discharge curve showing the relationship between the potential and the capacity per 1 g of elemental sulfur during discharging, and the broken line represents a charge curve showing the relationship between the potential and the capacity per 1 g of elemental sulfur during charging.

[0061]

The initial specific discharge and charge capacities were 263 mAh/g, and 243 mAh/g, respectively. This suggests that the elemental sulfur was charged/discharged reversibly. Moreover, in Inventive Example involving the process of

impregnating the positive electrode with the electrolyte,
both the specific discharge and charge capacities were
increased, compared with those in Comparative Example without
the process. The result shows that the positive electrode
5 was impregnated with the non-aqueous electrolyte the positive
electrode due to the process of impregnation, leading to the
further increased specific charge/discharge capacity.

[Brief Description of the Drawings]

[FIG.1]

10 A schematic diagram for use in explaining a test cell
prepared in each of Inventive Example and Comparative Example
of this invention

[FIG.2]

A diagram showing the measurement results of initial
15 charge-discharge characteristics of the test cell of
Comparative Example

[FIG.3]

A diagram showing the measurement results of initial
charge-discharge characteristics of the test cell of
20 Inventive Example

[Description of Reference Numerals]

10 Test cell vessel
11 Working electrode
12 Counter electrode
25 13 Reference electrode

14 Non-aqueous electrolyte

Fig. 1

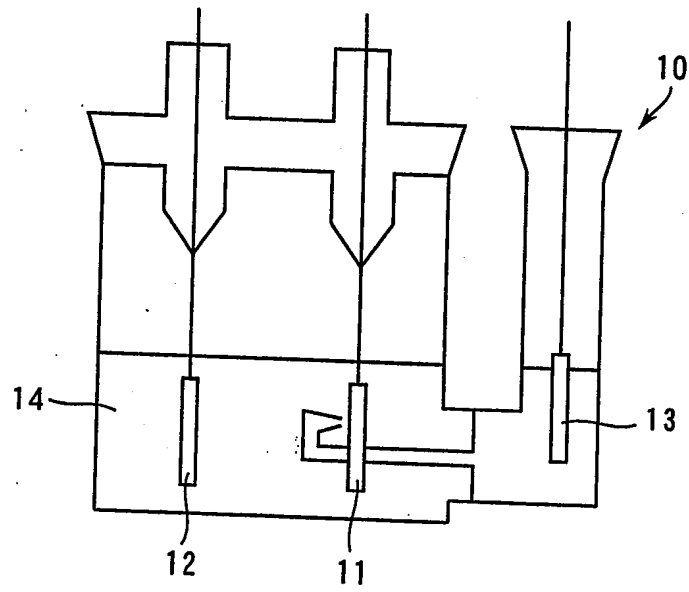


Fig.2

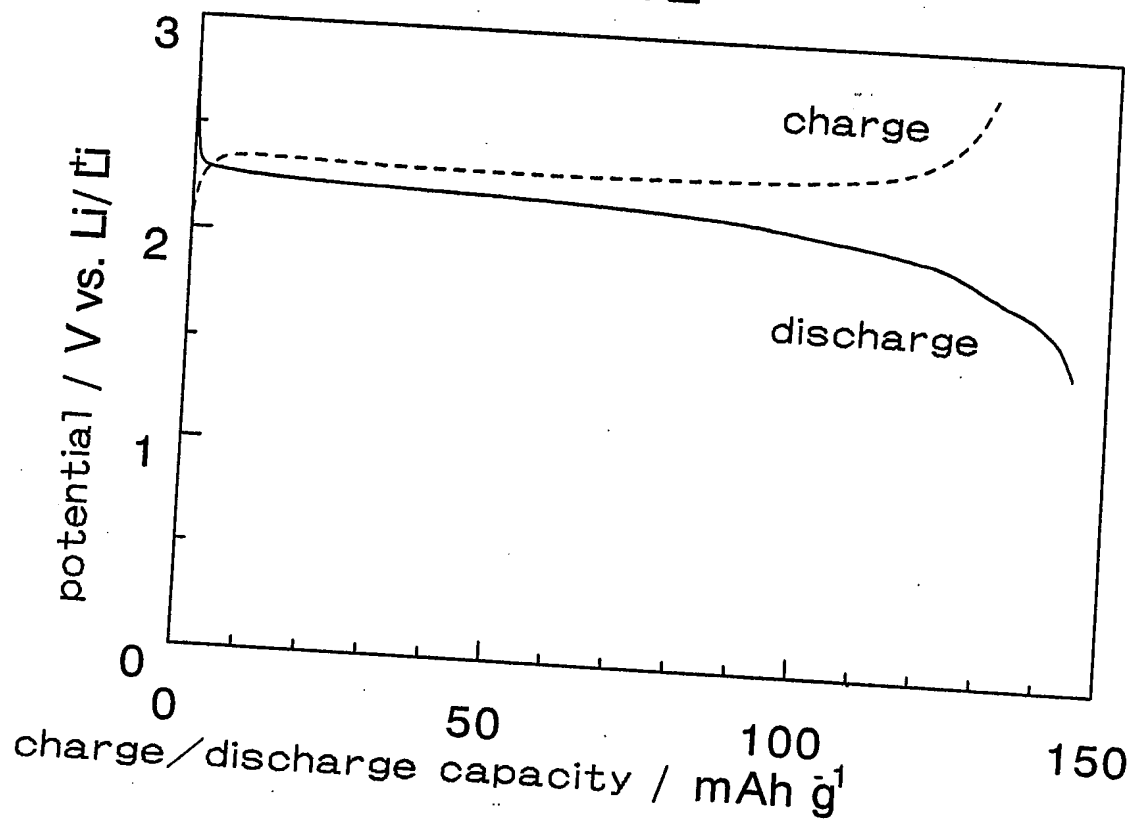
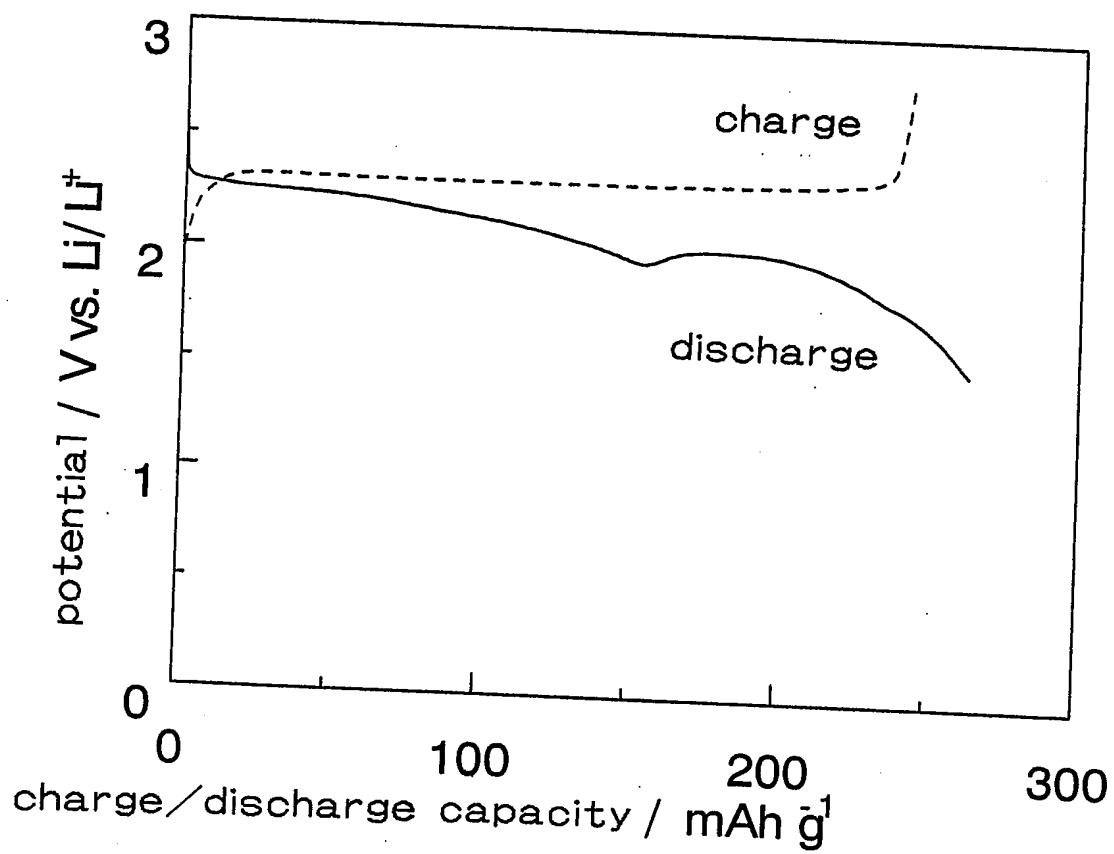


Fig. 3



[Document Name] Abstract

[Abstract]

[Subject] A method of manufacturing a positive electrode having increased energy density by the use of sulfur and a non-aqueous electrolyte secondary battery comprising the same are provided.

[Solving Means] A non-aqueous electrolyte secondary battery is composed of a negative electrode, a positive electrode, and a non-aqueous electrolyte. The positive electrode has a positive electrode active material made of a mixture of elemental sulfur, a conductive agent, and a binder. The electrode having a positive electrode active material is processed under reduced-pressure while immersed in the non-aqueous electrolyte. A pressure during the reduced-pressure process is preferably not higher than 28000 Pa (- 55 cmHg with respect to atmospheric pressure). As the non-aqueous electrolyte, a non-aqueous electrolyte including a room temperature molten salt having a melting point of not higher than 60°C and a lithium salt may be used.

[Selected Drawing] Fig. 1